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A METHOD OF CHROMATOGRAPHIC DETERMINATION OF ACROLEIN IN THE PRESENCE OF ALIPHATIC ALDEHYDES

[Metod khromatograficheskogo opredeleniya akroleina v prisutstvii alifaticheskikh al'dehidov]

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A METHOD OF CHROMATOGRAPHIC DETERMINATION OF ACROLEIN IN THE PRESENCE OF ALIPHATIC ALDEHYDES

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We have tested methods used in industrial-sanitary chemistry (see table) and have come to the conclusion that none of the colorimetric methods is suitable to analyze acrolein in the presence of aliphatic aldehydes and nitrogen oxides.

The nonspecificity of these methods compelled us to turn to chromatographic determination of aldehydes. Best known is the method of studying carbonyl compounds with 2.4-dinitrophenyl (2.4-DNP) hydrazine. This method makes it possible to analyze aldehydes both in the air of industrial plants and in exhaust gases. However, literature data and our own experimental material indicate that this method is insufficiently sensitive and the R_f of 2.4-DNP hydrazines of acrolein, acetaldehyde and formaldehyde are very close to each other. In addition, 2.4-DNP hydrazine produces derivatives with all carbonyl compounds whose number in break-down products of high-molecular compounds can be very great and deciphering these chromatograms is very difficult.

We were not able to use any of the tested methods of determining aldehydes to study acrolein, which in the overwhelming majority of cases is found in mixtures with other aldehydes in break-down products of high-molecular substances and products of incomplete fuel combustion. We turned to the method of Alarkon, based on the interaction of acrolein and m-aminophenol in a hydrochloric medium. As a result of the reaction a condensation product is formed which is brightly fluorescent in ultraviolet rays and is identified by the author as 7-oxyquinoline. We proved this method; its high sensitivity was verified. But the m-aminophenol solution is unstable in storage; therefore, we tested a number of animophenols and phenylenediamine. The most suitable was m-phenylenediamine, whose sensitiv-

ity was slightly higher than m-aminophenol; its solution is more stable in air and the 7-aminoquinoline which forms, evidently, as the result of the reaction with acrolein, is easily extracted from an alkaline medium with organic solvents.

Characteristics of several methods of determining aldehydes

Reagent	Sensitivity of aldehydes (in µg)			Mixing substances
	formaldehyde	acetaldehyde	acrolein	
Fuchsine-sulfur reagent	2	10	10	Oxidants. Nitrogen peroxide. Excess for formaldehyde in an acid medium.
Chromotropic acid	0.5	--	5	Nitrogen peroxide with 5 µg. Unsaturated and other compounds giving color with sulfuric acid. Phenol 2 µg
Tryptophan	10	100	2-5	Nitrogen peroxide. Formaldehyde reduces color with concentration of 2 µg, acetaldehyde with 20 µg
Dimethyl aminobenzaldehyde	--	5	5	Nitrogen peroxide.
4-Hexylresorcinol	--	--	1	Nitrogen peroxide 5 µg. Crotonic aldehyde 2 µg. Violet color.
Separate determination of formaldehyde and acrolein (Gronsberg)	0.5	--	5	Unsaturated compounds. Nitric oxides. Phenol 2 µg

On the basis of this reaction a method was developed to determine acrolein in the presence of acetaldehyde, and crotonic aldehyde in the air of industrial plants and in atmospheric air. We tested several liquid and solid absorbent media, as the result of which we came to the conclusion that the best absorbent solution for acrolein is 0.25% solution of hydrochloric hydroxylamine with air

sampled at the rate of 0.5 l/min and AG-5 charcoal sampled at a rate of 1 l/min.

To determine the maximum single concentration of acrolein in the atmosphere tested air is drawn through a four-bulb glass tube filled with AG-5 activated charcoal at a rate of 1 l/min for 50 minutes. Two grams of activated charcoal, first treated with acids, are placed in each tube. It is desirable to study the samples the day they are taken, but if this is not possible they can be kept in a refrigerator. Aldehydes are repeatedly extracted from the charcoal with a 0.25% solution of hydrochloric hydroxylamine; all extracts are filtered through a paper filter into one test tube. Further analysis of samples, taken in a 0.25% solution of hydroxamine and in charcoal, is conducted in the same way. For analysis are taken all filtrates obtained in the treatment of the charcoal, or all the absorbing liquid (4 ml), if the samples are taken in a Zaytsev absorber (liquid from each absorber is analyzed separately). At the same time a "witness" solution is prepared. For this 0.2 ml of a standard solution of acrolein (2µg/ml), 0.2 ml standard solution of acetaldehyde (200 µg/ml) and 0.10 ml standard solution of crotonic aldehyde (50 µg/ml) are placed in the colorimetric test tube. The volume of liquid is brought to 4 ml with a 0.25% solution of hydrochloric hydroxylamine.

The control solution contains 4 ml of the hydroxylamine solution. Then 1 ml of 1% solution of m-phenylenediamine and 1 ml of 5 n solution of hydrochloric acid are added to the "witness," the control solution and the test tube with the samples. The test tubes are placed in a boiling water bath for 10 minutes. After cooling 0.5 ml of 25% solution of ammonia is added to each test tube and repeatedly extracted with chloroform (3 times, 1-1.5 ml each). The chloroform extracts are filtered through a dry filter into dry test tubes and the chloroform is removed in a water bath at 65-70°. The dry residue is dissolved in 0.1 ml of chloroform, from which 0.05 ml is applied to the starting line (1 cm from the edge of the plate) of a chromatographic silufol plate (or prepared on the basis of 5 g of silicagel KSK, 0.5 g gypsum and 20 ml water). The sample, the control and the "witness" are applied to one plate 1 cm from each other. After the evaporation of the chloroform, the plates are placed in a chromatographic chamber saturated with vapors of the liquid phase.

For chromatographic separation of these aldehydes 2 solvent systems are recommended. One — quickly separating (ethylene alcohol-chloroform 1:4), R_f of acrolein in this system is 0.7, acetaldehyde and crotonic aldehyde — 0.43. The second system — slowly separating (isopropyl alcohol-acetic acid-water 12:0.5:5). R_f of acrolein is 0.47, acetaldehyde — 0.34. In the presence of several substances in the air reacting with m-phenylenediamine (acrolein, acetaldehyde, methylvinylketone, crotonic aldehyde, methylmercaptopropion aldehyde), it is preferable to use the second solvent system. After the line of the front rises to the edge of the plate (15 cm) it is extracted, dried in air and examined in ultraviolet light. The spots are mounted with pins and their R_f measured. Sections of silicagel with spots (control and samples) are removed to test tubes, over the silicagel is poured 6 ml of 1 n solution of hydrochloric acid. The liquid settles or is filtered and the intensity of green fluorescence measured in a fluorimeter with yellow light filters: 1 n solution of hydrochloric acid is determined at 6% according to the scale of the instrument. The amount of acrolein in the sample is found according to a calibrated graph.

CONCLUSIONS

1. A fluorescent method of determining acrolein has been developed, based on its interaction with m-phenylenediamine in a hydrochloric medium with the formation of a brightly fluorescent reaction product. The sensitivity of determination — 0.05 μg of acrolein in 5 ml.

2. A method of separating and quantitatively determining acrolein has been developed with the aid of thin-layer chromatography in silicagel-gypsum. Two solvent systems are recommended. The first system: ethyl alcohol-chloroform (4:1); R_f of acrolein is 0.7; the second system: isopropanol-acetic acid-water (12:0.5:5); R_f of acrolein 0.47. Quantitative determination is made fluorometrically after the extraction of derivative acrolein from silicagel. Sensitivity — 0.1 μg of acrolein in a specified volume.

3. It has been established that formaldehyde, aromatic and saturated aliphatic aldehydes, amines, phenols and nitrogen peroxide do not disturb determination. Acetaldehyde and crotonic aldehyde are separated in chroma-

tography.

4. For the absorption of vapors of acrolein from the air a 0.25% solution of hydrochloric hydroxylamine and activated charcoal (AG-5) is recommended.